

extreme; small power is sufficient, and the inductive connection of the collector to the receiving instrument may be separated by a surprising interval without stopping communication.

6. Two sending instruments can work at once on the same aerial bisected electrically, and at the distant station two receiving instruments can receive independently and simultaneously from the corresponding halves of an aerial there.

7. Under these non-earthed conditions every other station, even near and powerful ones, can be tuned out and their disturbance eliminated.

8. The importance of the possession of power thus to hold conversation in the midst of disturbance, without being affected by it, and the naval danger of being without such power, are emphasised.

On the Influence of their State in Solution on the Absorption Spectra of Dissolved Dyes.

By S. E. SHEPPARD, D.Sc. (Lond.), late 1851 Exhibition Scholar.

(Communicated by Sir William Ramsay, K.C.B., F.R.S. Received March 9,—
Read March 18, 1909.)

In a previous investigation of the absorption spectra and sensitising properties of some *isocyanine* dyes,* the influence of the solvent was examined and it was found that the absorption maximum was shifted toward the red as the refractive index of the solvent increased. This is in accordance with Kundt's law. The absorption in water, however, differs markedly from that in organic solvents. In the latter the spectrum consists of a prominent band in the orange and a half-shade nearer the blue.† In water this half-shade has become a separate band comparable in intensity with the orange. Absorption curves in alcohol and water are shown.

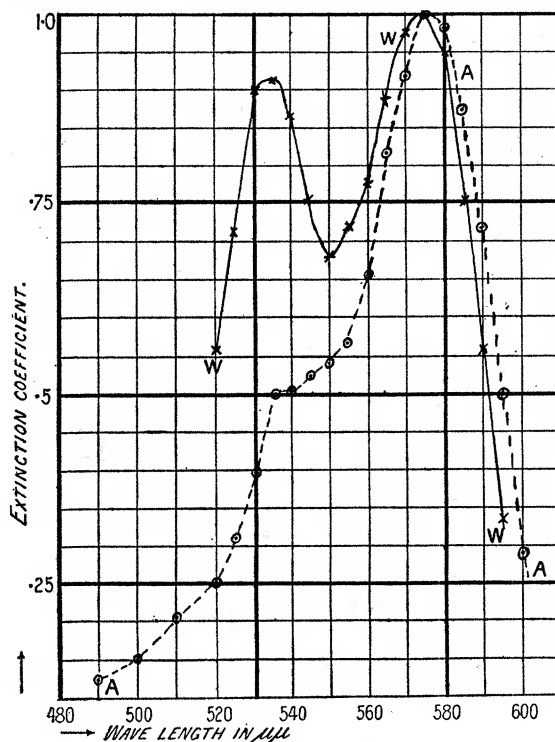
It is convenient to term the band near the red the β -(organic) band, the one nearer the blue the α -(water) band. It appeared desirable to investigate this difference further.

* 'Chem. Soc. Trans.,' vol. 95, 17 (1909), and 'Roy. Phot. Soc. Journ.,' vol. 48, p. 300, 1908.

† The α -band is at *ca.* 535 $\mu\mu$, the β -band at 575 $\mu\mu$; the positions depend on the isocyanine (*vide* papers quoted).

The Action of Alkali.

Aqueous solutions of the isocyanines are very sensitive to traces of acid, even the CO_2 from air being sufficient to discharge the colour. The change from a colourless to a coloured state is probably due to the salt formed having a different structure.* But whilst the first additions increase the colour, beyond a certain point further increase of alkali lessens the intensity of the α -band, whilst leaving that of the β -band relatively unaltered. This



CURVE 1.—Isocyanine.

W = absorption in water.

A = absorption in alcohol.

change in the ratio of the absorptions was followed spectro-photometrically, the instrument being an improved form of the Hüfner spectro-photometer.† In Tables I and IA measurements for two different isocyanines are given.

The action of alkali is complex and not easy to interpret. At first it increases the total absorption, which we may attribute to the formation of the true dye, tautomeric with the colourless form. The concentration of this in presence of excess of alkali should remain constant: actually the intensity

* This question is discussed in the papers cited.

† See 'Theory of Photographic Process' (Longmans, 1907), p. 28.

Table I.

Conc. of alkali, KOH.	Σ at 540 $\mu\mu$.	Σ at 587 $\mu\mu$.	Ratio.
Per cent.			
0.4	0.946	0.871	1.085
0.8	0.960	0.874	1.092
1.6	0.962	0.871	1.102
3.2	0.917	0.765	1.198
6.4	0.919	0.620	1.500
13.4	0.749	0.432	1.780
13.4 after 30 minutes	0.692	0.379	1.720

Table IA.

Conc. of alkali.	Σ at 535 $\mu\mu$.	Σ at 575 $\mu\mu$.	Ratio.
Per cent.			
—	0.244	0.361	0.675
0.2	0.440	0.537	0.82
0.5	0.510	0.598	0.855
1.0	0.541	0.533	0.962
2.0	0.502	0.473	1.065
4.0	0.505	0.420	1.190
8.0	0.511	0.374	1.370
16.0	0.490	0.262	1.850

Σ is the Bunsen extinction-coefficient, calculated from the relation $I = I_0 10^{-\Sigma d}$, where I and I_0 are the transmitted and incident intensities.

d , the thickness, in this case 1.00 cm. The concentration of the dyes was 1 in 100,000.

of the α -band remains constant, that of the β -band diminishes, over a certain range; ultimately above a certain concentration of alkali the solution becomes turbid. In alcohol no action of this nature could be observed—

Conc. of alkali 0 0.5 1.0 4.0 8.0 per cent.

Ratio $\Sigma\beta/\Sigma\alpha$ 2.27 2.16 2.20 2.23 2.23

This would seem to preclude the idea of a chemical modification. The increasing turbidity, amounting finally to precipitation, suggested that the change involved was one of aggregation, the dye being present in various stages of aggregation, from true solution to suspension, and that the alkali coagulated the finer particles. On this view the α -band is due to a suspension, the β -band to a colloidal solution, but one very near true solution. To test this hypothesis, the "solutions" were examined with the ultramicroscope. A Zeiss microscope was used with a paraboloid substage condenser,* being the second arrangement of Siedentopf and Zsigmondy,†

* For the principles and technique, see R. Zsigmondy, 'Zur Erkenntniss d. Kolloide,' Fischer, Jena, and A. Cotton and H. Mouton, 'Les Ultramicroscopes,' Masson et Cie., Paris.

† Cotton and Mouton, *loc. cit.*, p. 52.

and this parallel investigation of the state of aggregation was extended to other dyes.

For brevity, the results are expressed in tabular form, some are then discussed in greater detail :—

Table II.

Solvent.	Colour	Absorption maximum in $\mu\mu$.	Appearance in ultra.	Electrolytes.
<i>Isocyanine.*</i>				
Water	Reddish purple	535 and 575 ...	Large number of small granules	Increase in number and size of grains, especially KOH.
Alcohol	Purple	577, and half shade at 535	Few grains	No action.
Chloroform	Purple	583, and half shade at 540	Nearly optically clear	
<i>Cyanine (lepidine-cyanine).†</i>				
Water	Reddish violet	Max. at 560, ill defined	Many grains	Increase in number and size of grains.
Alcohol	Blue	605, well defined	Very few grains	No action.

* *p*-toluquinaldine-*p*-ethoxy-quinoline ethyl cyanine bromide.

† Lepidine-iso-amyl-cyanine.

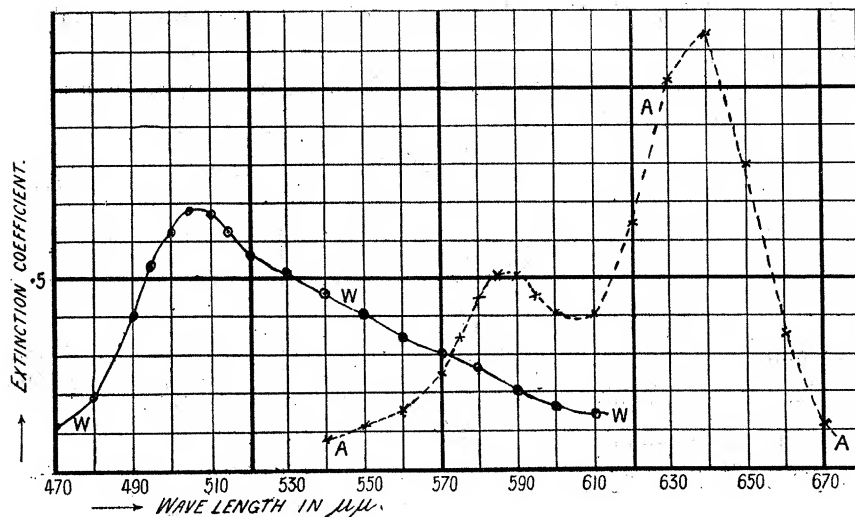
Table IIA.

Solvent.	Colour.	Absorption maximum in $\mu\mu$.	Appearance in ultra.	Electrolytes.
<i>Pinacyanol.* Curve 2.</i>				
Water	Rose-pink	505—510, flat, ill defined	Many grains, some greenish blue, others brilliant yellow. Small suspended crystals also	Conc. KCl gradually coagulates. KOH makes turbid. Absorption shifted.
Alcohol	Deep blue	640, strong; 587, weaker	Very few grains, much smaller†	No action.
Xylol	Deep blue	—	Very few grains	
Chloroform	Deep blue, but brighter	643, strong; 592, weaker	Optically clear	
Quinoline ...	Greenish blue	660, strong; 605, weaker	Very few small grains	
<i>Pinachrome blue.‡ Curve 3.</i>				
Water	Rose	535, flattish ...	Similar to pinacyanol	Coagulated. At first, shift of absorption.
Alcohol	Blue-green.....	650, strong; 595, weak	Very few grains	No action.

* The pinacyanols are dyes of unknown constitution, but allied to the isocyanines. The one used was from *p*-ethoxy-quinaldine.

† The size is judged from the brilliancy.

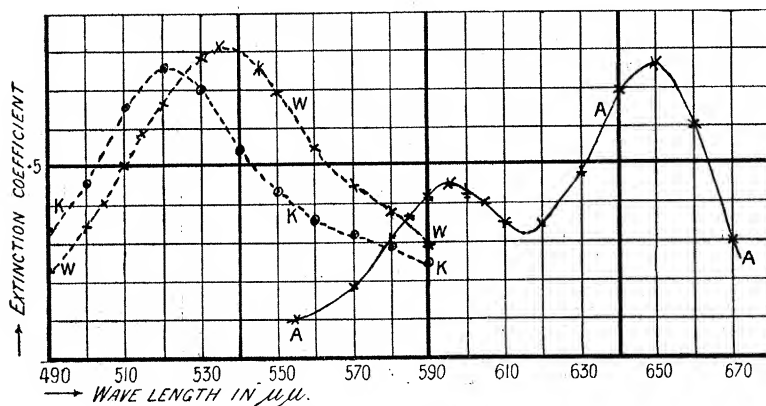
‡ Allied to the pinacyanols.



CURVE 2.—Pinacyanol.

A, 1 in 200,000 alcohol.

W, 1 in 100,000 water.



CURVE 3.—Pinachrome.

K = absorption in $n/50$ KCl.

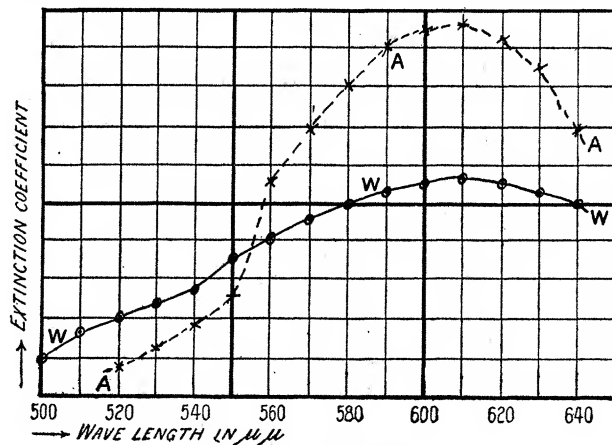
(To economise space, only the curves are given, and not the tables of extinction-coefficients.)

It is evident that the dyes are contained in quite different form in water and in alcohol, or organic solvents. The evidence that they are partially in suspension, partially in colloid solution, was as follows:—

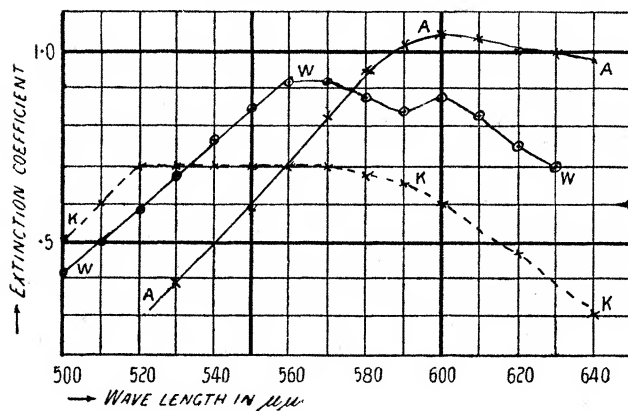
(a) They are coagulated by concentrated solutions of KCl, more rapidly by di- and trivalent cations, as Zn, Mg, Al. The process could be followed microscopically in the manner used by Linder and Picton with colloidal As_2S_3 .

Table III.

Solvent.	Colour.	Absorption maximum.	Appearance in ultra.	Electrolytes.
Sky-blue extra (Licht-blau). See Curve 4.				
Water ...	Blue	Ca. 610, band very broad	Many grains	Gradual coagulation.
Alcohol ...	Deep blue ...	610, band sharp and clear	Very few grains	No action.
Congo blue. See Curve 5.				
Water ...	Turbid blue	560, dip at 585, max. at 600	At $\frac{1}{10}$ per cent. many grains small, at $\frac{1}{100}$ per cent. few, but luminous field	Acid precipitates KOH, clears di- and trivalent cations precipitated.
Alcohol ...	Blue	Max. at 600, sharper shading to blue	Very few grains	



CURVE 4.—Licht-blau.



CURVE 5.—Congo blue.

K = absorption in 1 per cent. KOH.

(b) Aqueous solutions are coagulated by repeated heating and cooling, though not so completely as by electrolytes.

(c) The aqueous solutions show the Tyndall cone with an intense beam of light. The further ultramicroscopic appearance is given in the tables.

The remarkable difference in the absorption-curves of aqueous and organic solutions of pinacyanol and pinachrome blue is shown in the curves. Further, it is interesting to note that the addition of KCl in quantity insufficient to precipitate the dye immediately shifted the absorption still further toward the blue. This points to the particle-size as being one factor in modifying the absorption.

Colloid Solutions of Dyes.

Recent investigations have shown* that a very considerable number of dyes exist in pseudo- or colloid solution in water. Michaelis, from their ultramicroscopic appearance, divides them as follows :—

(a) Optically, completely resolvable, showing granules at the greatest dilutions. Such are many sulpho-dyes, as induline, violett-schwarz, aniline-blue.

(b) Partially resolvable, showing granules to an increasing degree above a certain concentration. Such are fuchsin, methyl violet.

(c) Not resolvable. Generally fluorescent. As fluorescein, toluidine blue, eosine.

From the experiments detailed above it would seem that *pinacyanol* and *pinachrome* blue belong to the first class, *cyanine* and *isocyanine* and *sky-blue extra* to the second. But all pass into the third in organic solvents, and the important point is, that *this change in the state of aggregation is accompanied by a marked change in the absorption spectrum*. It appears that care must be exercised in correlating all colour changes with structural modifications.

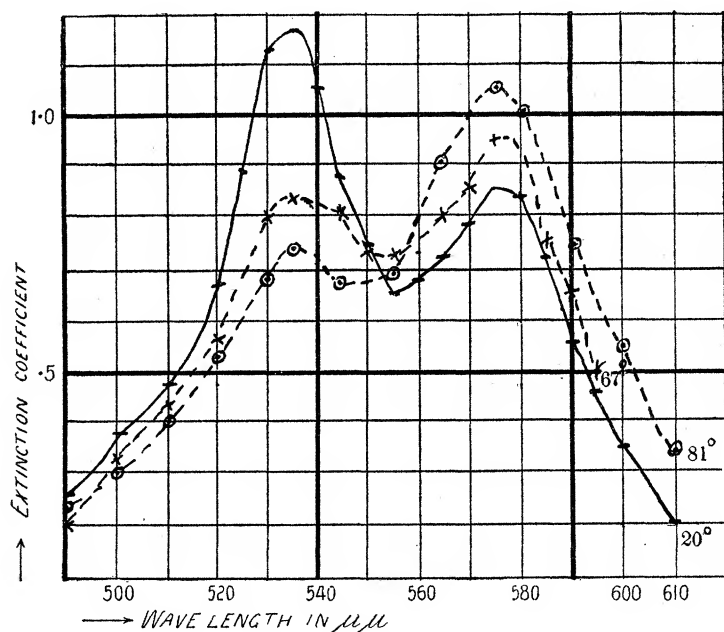
Action of Temperature.

Whereas so far the disaggregation producing true solutions was only obtained by changing the solvent, the important result was obtained that on heating the aqueous solutions of pinachrome, pinacyanol, *isocyanine*, and *cyanine*, the pseudo-solutions passed into the state of true solution, the colour gradually changing, and the optical heterogeneity disappearing. With pinacyanol the change appeared to be complete above 100°. The change was followed quantitatively for *isocyanine* and pinacyanol.

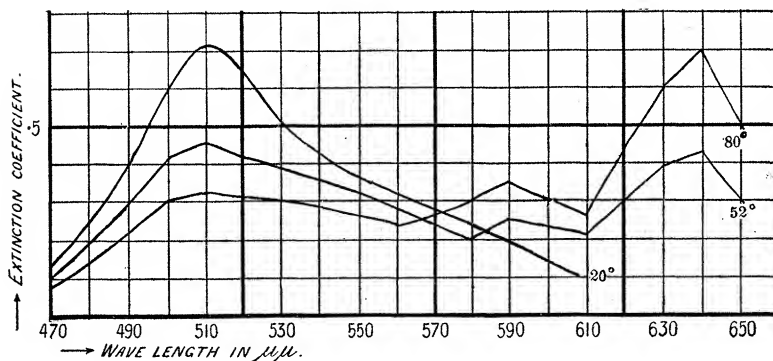
The Hüfner spectrophotometer not being quite suitable, a König instrument

* Cf. B. H. Buxton and O. Teague, 'Zeitschr. phys. Chem.,' vol. 60, p. 4, 1907 ; L. Michaelis, 'Virchow's Archiv,' vol. 179, p. 195, 1905.

was employed. The method was to compare two exactly similar solutions, one kept at 20° , the other heated to a known constant temperature. Two exactly similar tubes of 20 cm. length were constructed, the ends being closed with plate glass and having apertures for thermometers. One was heated by a coil of wire through which passed the lighting current; by means of a variable resistance any desired temperature up to 80° could be obtained, constant to $0^{\circ}.5$. One slit of the spectrophotometer was illuminated directly, the other by reflection from a right-angled prism, and this was effected by two Auer burners fed from the same gas tap. The readings gave



CURVE 6.—Isocyanine.



CURVE 7.—Pinachrome.

the differences between the hot and cold solutions. From the known extinctions for the cold solution at 20°, the curves for the different temperatures were constructed (curves 6 and 7).

It will be seen that there is a gradual transition from the spectrum of the pseudo-solution to that of the true solution as shown in alcohol (compare with curves 2 and 3). The change of temperature has precisely the same effect as the addition of an organic solvent miscible with water such as alcohol or acetone. *In the hot solutions very few grains were visible and electrolytes had no effect. On cooling, the solutions returned to their former colour and state.* The phenomena are similar to the behaviour of starch, which at or above the boiling point of water gives true crystalloid solutions of high molecular weight,* showing in the ultra-microscope only the diffuse beam due to "amicros," or particles too small to be rendered visible.† On cooling, the starch solution becomes opalescent. The behaviour is characteristic of reversible colloids forming at high temperatures unsaturated crystalloid solutions, at low ones very supersaturated and colloidal ones.‡ Apparently the pinacyanols and probably other dyes belong to this class, *i.e.*, they spontaneously dissolve in water to a colloid solution, or reach a very fine state of division but one still remote from molecular dimensions. It is possible that this change of aggregation may in part account for some of the interesting changes in the absorption-curves of other dye solutions with change of temperature noticed by Nichols.§

Influence of Acid on Alkali.

Michaelis noticed that Nile blue sulphate and alizarin blue with soda lye give pseudo-solutions. A considerable number of dyes were found to change their degree of aggregation when acid or alkali was added, but there are of course in many cases chemical changes masking this. The dyes were also examined for electric transport, and the results were in agreement with the previous datum of V. Henri and A. Mayer,|| that OH' and H' ions flock or clear positive or negative colloids respectively.

Linder and Picton¶ noticed that Congo red in alkaline solution filters readily through a porous cell but was retained in neutral or acid solution. In the majority of cases there are undoubtedly chemical changes, but these are accompanied or preceded by changes in the state of aggregation.

* Cf. Lobry de Bruyn, 'Rec. Chim. Trav.,' vol. 19, p. 253, 1900.

† R. Zsigmondy, *loc. cit.*, p. 87.

‡ *Ibid.*, p. 163.

§ 'Zeitschr. phys. Chem.,' vol. 48, p. 271, 1900.

|| 'C. R. Soc. Biol.,' vol. 55, p. 1671, 1903.

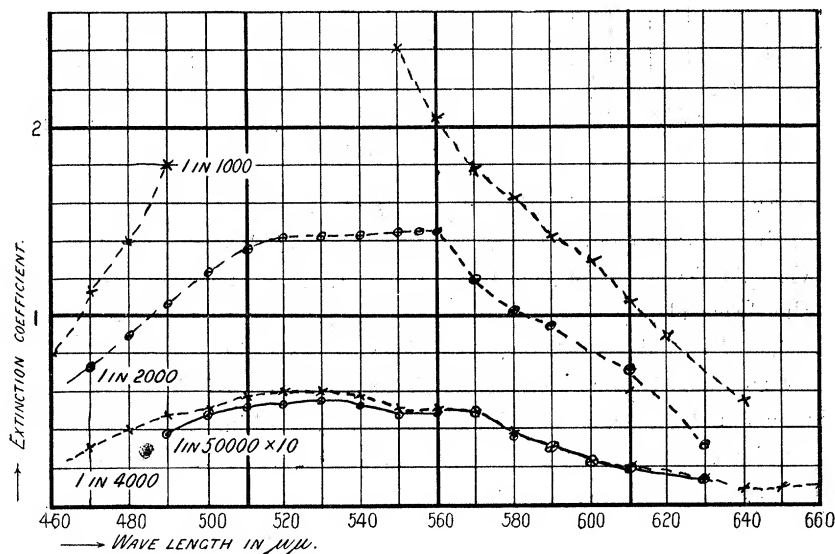
¶ 'Chem. Soc. Trans.,' 1892, p. 148.

Table IV.

Dye.	Acid.	Alkali.	Transport.
Pinachrome	Clears, finally decolorises	Turbid	+ ive colloid.
Pinacyanol	Ditto	"	+ ive "
Isocyanine	Decolorises	"	+ ive "
Sky-blue ex.	Turbid	Clears	- ive "
Dianil blue	"	"	- ive "
Congo blue	"	" turns red	- ive "
Bordeaux B	" but decolorised	"	- ive "
Benzopurpurin	"	Clearer	- ive "
Daphen blue	Clears	Turbid	+ ive "

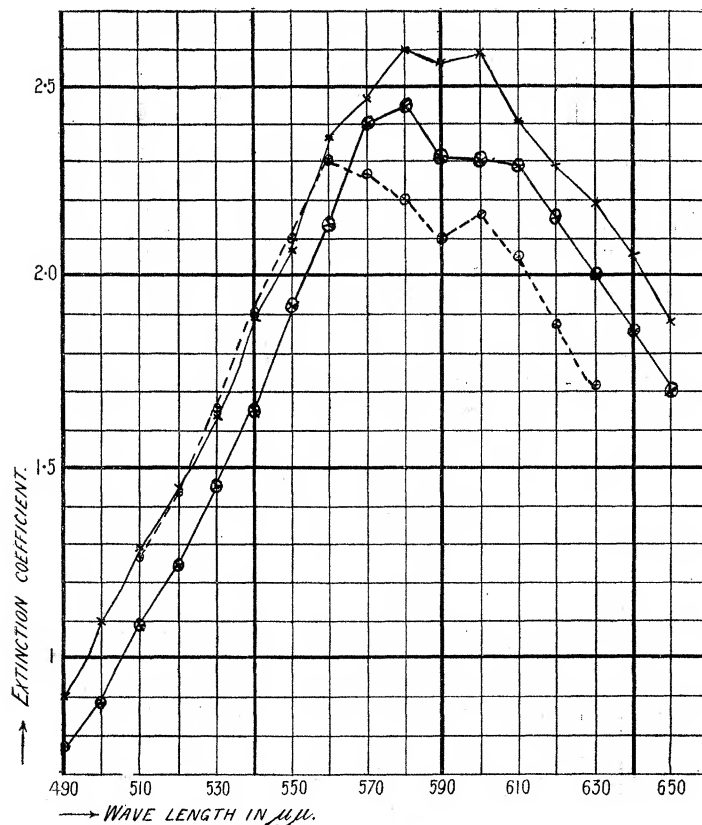
Influence of Concentration.

With the partially resolvable dyes (*v. p.* 262), the more concentrated the solution the greater the number of granules, dilution favouring the process of disgregation and solution. Optically it results that certain deviations of the absorption spectrum occur. The absorption curves for Bordeaux B and congo blue are given for different concentrations.



CURVE 8.—Bordeaux B.

The absorption in concentrated solutions, especially in the red, is *greater* than if Beer's law held.



CURVE 9.—Congo Blue.

The curves should coincide, if Beer's law held.

From these and other measurements it is concluded:—

(a) Completely optically resolvable dyes, *i.e.*, such as are in true solution, show the least change in the form of the curves; the maxima are not displaced. If chemically stable, Beer's law is followed.*

(b) Dyes partially in colloid, partially in true solution or complete solution, show deviations, sometimes displacement of maxima, at very high concentrations. These results are in agreement with the observations of Kalandek.†

The State of Dyes in Membranes.

Since the absorption-spectrum shows itself to some extent as a criterion of the state of aggregation in liquid "solutions," it is an obvious step to apply it to the investigation of the state of dyes in solid media. In the course of

* See paper in 'Chem. Soc. Trans.,' *loc. cit.*, p. 16.

† 'Physik. Zeitschr.,' 1908, May.

the present investigation, the "colloidal" of the dyes was tested by their dialysis through collodion sacs, prepared according to Malfitano.* It is interesting to note that a definite osmotic pressure was obtained with certain colloid dyes, persistent after sufficient dialysis to have removed crystalloid impurities. The dyes were: congo blue, aniline blue, primuline, all resolvable optically. That such colloids can show a definite osmotic pressure has already been shown by Linder and Picton, and by R. S. Lillie.† Other colloid dyes were completely absorbed by the collodion, as pinacyanol. And here the interesting fact was observed, that the dye, in pseudo-solution in water, gave the colour and absorption spectrum of the true solution in collodion.

The following table gives a brief survey of some of the absorption results. The degree of absorption is indicated thus: + = strongly, *m* = moderately, — not absorbed. In addition, the nature of the spectrum is noted, corresponding to pseudo- or true solution.

Table V.‡

Dye.	Collodion.	Viscose.	Gelatine.	Caoutchouc.
Pinacyanol	+, bands as in alcohol	+, bands as in alcohol	—	<i>m</i> , spectrum as in water.
Pinachrome	Same as pinacyanol.			
Congo blue	+, band as in alcohol	...	+, band as in water	—
Rosaniline	+	+	+	+
Isocyanine (alkaline)	+, bands as in alcohol	+	—	<i>m</i> , uncertain.
Crystal violet	+, band as in water	+	+	
Sky-blue ex.	+, as in alcohol	+	+	—

It is impossible to draw general conclusions as to the behaviour of membranes from these few experiments, a behaviour which appears to depend on a great variety of specific factors,§ but the important point is that in certain cases the dye is truly dissolved.

This lends a certain amount of support to the view that in osmosis the membrane acts as a *solvent* for the permeating substance. Returning to the absorption of dyes, colloid membranes themselves possess a charge,|| and

* 'C. R.,' vol. 139, p. 1221, 1904.

† 'Amar. Journ. of Physiol.,' vol. 20, p. 167, 1907.

‡ *Collodion* is nitro-cellulose, *viscose* = xantho-cellulose, the *caoutchouc* was pure rubber from coagulated latex.

§ Cf. H. Zangger, 'Vierteljahr. Naturforsch. Ges. Zürich,' vol. 51, p. 432, 1906.

|| Cf. V. Henri and A. Icovesco, 'C. R. de la Soc. de Biol.,' vol. 51, p. 197, 1906.

this appears to be an important factor in absorption. Collodion is negative to water, and this agrees with its strong absorption of positive colloids such as pinacyanol, but it does not explain the solution thereof. Gelatine is +ive or -ive according to the alkalinity or acidity of the solution in contact. I have tested the absorption of a large number of dyes in neutral solution with a carefully dialysed gelatine, therefore as neutral as possible. Here the colloidality of the dye appears to play a great rôle, *i.e.*, the more colloidal the less absorbed (see Table VI), but an absolute generalisation this is not.

Table VI.

Dye.	Colloidality by dialysis and ultra.	Absorption by gelatine.	Absorption by caoutchouc.	Spectrum in water.
Naphthol green	Little or <i>nil</i>	+	<i>m</i>	Well defined.
Methylene blue	"	+	<i>m</i>	Steep.
Indigo carmine	"	+	+	"
Chrysaniline	"	+	<i>m</i>	"
Crystal violet	Slight	+	+	"
Rosaniline	"	+	+	Sharp.
<i>Janus yellow B</i>	"	+	<i>m</i>	"
Isocyanine	Moderate	<i>m</i>	—	"
Cyanine	"	<i>m</i>	—	Diffused.
Bordeaux B	"	+	...	Ill defined.
Cœrulein	"	—	...	"
Sky-blue ex.	"	<i>m</i>	—	"
Congo orange	"	+	—	"
Congo blue	Strongly	+	—	"
Nigrosine	"	—	—	"
Wool blue 5B	"	Slightly	—	"
Pinacyanol	"	—	<i>m</i>	Flattish.
Pinachrome	"	—	<i>m</i>	"
Benzopurpurin B	"	<i>m</i>	—	"
Aniline blue	"	<i>m</i>	—	"

The Action of Dyes on each other's Absorption Spectrum.

Colloid dyes of opposite sign may form so-called "complex colloids" stable in excess of one component.* An interesting phenomenon was noticed with Baumwoll-gelb S and pinacyanol—

Solution.	Absorption spectrum.
Pinacyanol in cold water.	Band at $510\ \mu\mu$.†
" hot water.	Bands at $590\ \mu\mu$ and $640\ \text{mm}$.†
Baumwoll-gelb S.	Absorption in blue, violet, and ultra-violet (max.).
Pinacyanol in excess of Baumwoll-gelb S.	Bands at $510\ \mu\mu$, $590\text{--}600\ \mu\mu$, and at $660\ \mu\mu$.

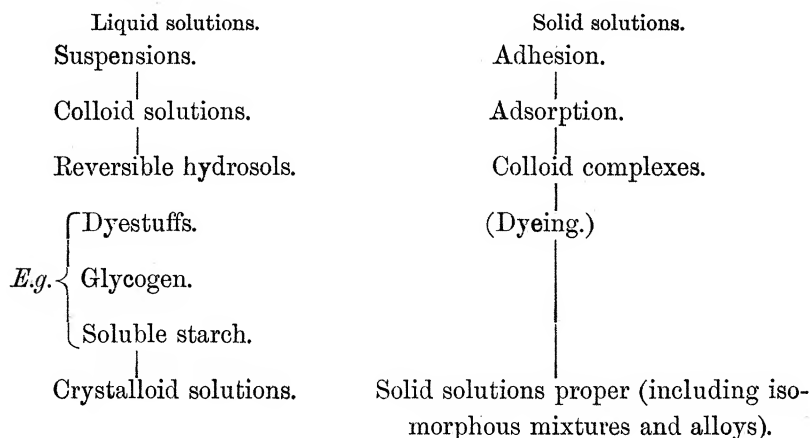
* Cf. B. H. Buxton and O. Teague, 'Zeit. physik. Chem.,' vol. 50, p. 479, 1907.

† See Curve 2.

Now we have found the bands at *ca.* 590 and 640 $\mu\mu$ as characteristic of true solution, so that it appears, that just as in membranes, one component in so-called "complex-colloids" may be partially in true solution in the other. Spectrophotometric examination of other complexes should yield valuable information as to the nature of this union.

Dyeing and the Nature of Solution.

The experiments detailed here seem to support the view that "solution" is a continuous phenomenon, from mechanical suspension down to true solution (Linder and Picton, Zsigmondy, and others). The author is of the opinion that the process of dyeing in solid media is strictly analogous to the "solution" of dyes in liquid solvents, in that all phases or grades may be found. It seems permissible to parallel the solution states in liquid and solid media as follows:—



In solutions of dyes, either in liquid or solid media, all grades may coexist, the conditions for forwarding or diminishing the degree of solution may be grouped as follows:—

Toward true solution.	De-solution.
Diminishing particles.	Increasing particles.
Dilution.	Concentration.
Admixture of other solvent.	Electrolytes.
Acid or alkali.	Alkali or acid.
Rise of temperature.	Lowering of temperature.

These conclusions are not novel,* but it seems worth while to point out that concomitant with "solution," in this sense, the absorption spectrum

* In particular, cf. R. Zsigmondy, 'Zur Erkenntniss d. Kolloide' (Fischer, Jena), and C. Dreaper, 'The Chemistry and Physics of Dyeing,' 1906.

tends to change from broad and ill-defined bands (*cf.* Licht-blau, p. 261) to sharp ones, whilst in certain cases a quite new spectrum is formed. (I hope to point out elsewhere the resemblance between the absorption spectra of colloid dyes and those of colloid metals, such as gold.) At the same time it appears probable that there is a progressively increasing combination between the "solute" and the solvent.

SUMMARY.

(a) In the aqueous solutions of certain dye-stuffs—iscyanines, pina-cyanols, cyanine—the dye is present partially or wholly in colloid solution, and the absorption spectrum is quite different from that of the true solution. The influence of various agencies, as heat, acid and alkali, electrolytes on the absorption was examined quantitatively.

(b) In other dye solutions, the change from true solution to the colloid state is accompanied by broadening and diffusion of the absorption curve, consequent on the increase in number and size of the colloid particles. Deviations from Beer's law result.

(c) The state of dyes in solid media is comparable with that in liquid, and the absorption spectrum is similarly affected. The absorption of a number of dyes by membranes was studied.

(d) The solution of dyes appears to be a combined process of disaggregation of the solute, accompanied by a progressive combination with the solvent. If the same stage of solution is attained in *different* solvents, the absorption maxima are displaced according to Kundt's law.

This investigation was carried out in the spring and summer of 1908 in the laboratory of Physiological Chemistry of the Sorbonne, Paris; the author desires to express his great thanks for the hospitality and facilities afforded him: in particular to the director, Prof. Dastre, and to M. Victor Henri for his continuous advice and interest.
